



A new palladium chelate compound for determination of sulfide

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ABSTRACT

A new palladium chelate compound is described for the determination of sulfide in aqueous samples. The reagent, bis(2-aminobenzoate)palladium(II) (PdA₂), was prepared by reaction of tetrachloropalladate (PdCl₄⁻) with 2-aminobenzoic acid. The compound was characterized by infrared spectroscopy and CHN elemental analysis. The measurement was based on the selective reaction of PdA₂ with sulfide in an aqueous medium, which quantitatively produced fluorescent 2-aminobenzoate ($\lambda_{\text{ex}} = 245 \text{ nm}$, $\lambda_{\text{em}} = 410 \text{ nm}$). The analytical response was linear in the range 0.10–20.0 $\mu\text{mol (S}^{2-}\text{) L}^{-1}$ ($r > 0.99$), with a limit of detection of 0.075 $\mu\text{mol L}^{-1}$ and repeatability (RSD) of 3.4%. There was no interference from CO₃²⁻, NO₃⁻, Cl⁻, SO₄²⁻, Br⁻, NO₂⁻, K⁺, NH₄⁺, Na⁺, citrate or S₂O₈²⁻. The fluorescence intensity decreased in the presence of H₃CCOO⁻, PO₄³⁻ and SCN⁻, while OH⁻ caused a positive interference. The new fluorescent compound was successfully applied for the determination of sulfide in synthetic wastewater and natural water sample. The advantages of the proposed palladium chelate are absence of toxic by-products, simple synthesis procedure of reagent and yield reaction of about 85%, easy handling and fast acquisition of analytical signal.

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1. Introduction

Hydrogen sulfide (H₂S) and other reduced sulfur compounds occur naturally in the environment and can be produced under anaerobic conditions in industrial processes [1,2]. H₂S is released during petroleum and natural gas extraction and refining [3], while large quantities of sulfide are formed by bacterial reduction of sulfate during the degradation of organic matter present in sewage [4]. Sulfide attacks metals and concrete, and causes corrosion on pipe walls [5]. Monitoring of sulfide in water is required in order to avoid any toxic effects on humans and aquatic organisms [6].

In the environment, sulfide is found in a wide range of concentrations ($\mu\text{g L}^{-1}$ – mg L^{-1}), as a result of which a variety of analytical methods for its quantification and monitoring have been reported. These range from classical techniques [7,8] to optical methods [6,9–12], electrochemistry [13–15] and separation procedures such as chromatography [16–18] and capillary electrophoresis [19]. Although some of these techniques are selective and are able to separate the components of a sample, the requirement for expensive and complex instrumentation makes most of them unsuitable for routine applications. For use where knowledge of total S²⁻ is sufficient, optical methods are particularly advantageous from the perspectives of equipment costs and analyst training requirements. Most of these methods require a preconcentration step, often using cadmium or mercury compounds. Reactions that produce dyes are the basis of colorimetric methods and can be adopted for automated instrumental measurement of sulfide [20]. Chemiluminescence and

fluorescence increase sensitivity without losing the benefits of low cost and fast detection. However, chemiluminescence reactions are affected by a variety of species including metals, anions, oxidants and organic compounds [21]. Yang et al. [22] developed a highly sensitive fluorogenic chemodosimeter for sulfide, employing its reaction with 2,4-dinitrobenzenesulfonyl-fluorescein, a weakly fluorescent compound, resulting in the formation of highly fluorescent fluorescein.

Mercury-complexing agents, such as alkaline fluorescein mercuric acetate (FMA), have been employed for the determination of sulfhydryl groups [23]. This well-known and sensitive reaction results in the quenching of FMA fluorescence. However the disadvantage of mercury, which is an efficient reagent for the collection of sulfide, is its high toxicity. The synthesis and analytical use of these organometallic compounds generate mercury-containing wastes whose disposal is problematic. Erwan Galardon et al. [24] synthesized zinc complexes with properties of colorimetric “turn-on” and fluorescence “turn-off” which showed high selectivity for hydrogen sulfide in the presence of thiols. However few experiments to characterize the analytical properties of the compounds were made. Similarly a heterobimetallic ruthenium(II)-copper(II) complex-based luminescent chemosensor was proposed to determine the sulfide [25]. This luminescence sensor showed an excellent selectivity and sensitivity response in a widely pH range from 4.5 to 10. However the synthesis of the reagent requires three laborious steps, involving various solvents, inert atmosphere, and three stages of purification and with yield reaction of about 36%. This fact can limit the widespread use of reagent by analytical laboratories.

Palladium is one of the most versatile of the transition metals and can coordinate with electron donor atoms such as N and O. The

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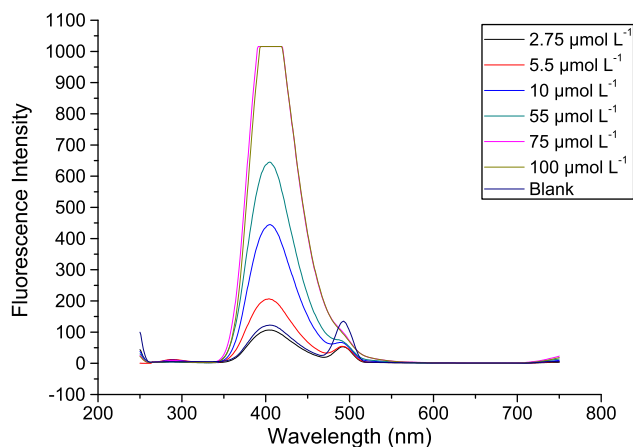


Fig. 1. Emission spectra of the palladium complex in methanol, acquired 20 min after addition of different amounts ($\mu\text{mol L}^{-1}$) of sulfide.

low-spin d^8 Pd(II) ion has the highest formation constant with heavy halide and sulfur ligands [26]. Palladium (II) ions form stable complexes with a variety of sulfur compounds, and the reaction has been employed for the quantitative determination of disulfides, thioethers and thiols [27].

Here, we propose the use of bis(2-aminobenzoate)palladium(II) complex (PdA_2) for detection of sulfide in aqueous solution. The synthesis of the compound is simple and involves only one step in the formation of (PdA_2) complex. In an aqueous medium, the presence of the sulfide causes formation of PdS and with dissolution of the highly fluorescent 2-aminobenzoate anion. The resulting increase in fluorescence intensity is proportional to the concentration of sulfide present in the solution and is the basis of the sulfide determination.

2. Experimental

2.1. Apparatus

The fluorescence spectra and relative fluorescence intensities were measured using a spectrofluorimeter (Model RF-1501, Shimadzu, Japan) fitted with a 10 mm quartz cuvette. The excitation and emission wavelength bandpasses were 10 nm. Infrared spectra of PdA_2 and 2-aminobenzoic acid were recorded using a Nicolet Impact 4000 FTIR spectrophotometer and KBr pellets. A Perkin-Elmer CHN 2400 instrument was used for elemental (C, H and N) analysis of the product. NMR spectra were recorded on a Varian INOVA-500 spectrometer. Chemical

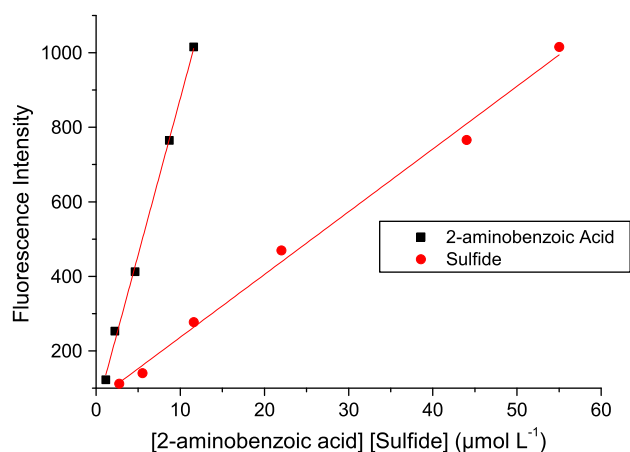


Fig. 2. Comparison of the fluorescence intensity of 2-aminobenzoic acid and reaction of PdA_2 with sulfide at different concentrations.

shifts were given in δ (ppm) relative to tetramethylsilane (TMS) as internal standard.

2.2. Reagents and solutions

2.2.1. Synthesis of the palladium-2-aminobenzoate complex (PdA_2)

The preparation of the palladium-2-aminobenzoate complex was based on the procedure described previously [28]. 117.6 mg of PdCl_2 (0.663 mmol) and 90.3 mg of NaCl (1.543 mmol) were suspended in 10 mL of deionized water with stirring for 4 h until a clear solution was obtained. 185 mg of 2-aminobenzoic acid (1.350 mmol) was dissolved in 5 mL of methanol and added dropwise to the first solution. This reaction mixture was stirred for 24 h. The brown-yellow compound obtained was filtered and then washed sequentially with copious amounts of water, methanol and *n*-heptane. The compound was air-dried, giving a final yield of 83%. $^1\text{H-NMR}$ (500 MHz, DMSO-d_6): δ : 6.49–6.46 (m, 2H), 6.71 (dd, $J=8.5, 1.0$ Hz, 2H), 7.39–7.36 (m, 2H), 7.74 (dd, $J=8.0, 1.5$ Hz, 2H). The percentage composition values obtained were 43.68, 3.14 and 7.28 for C, H and N, respectively. These were in good agreement with calculated values for $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_4\text{Pd}$ (PdA_2): of 44.17 (C), 3.71 (H) and 7.36 (N).

2.2.2. Reagents and standard solutions

All reagents were analytical grade. Solutions were prepared using deionized water (Milli-Q system, Millipore, USA) and methanol (J.T. Baker, Mexico). Sulfide stock solutions (0.010 mol L^{-1}) were prepared weekly by dissolving an appropriate mass of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (Synth, Brazil) in water. The sulfide salt was washed with water to remove surface impurities and dried with tissue paper. This solution was standardized by iodometric titration [29]. For the Methylene-Blue method [29], 0.27% (m/v) amine-sulfuric acid and 25% (m/v) ferric chloride solutions were prepared by dissolving an appropriate mass of *N,N*-dimethyl-*p*-phenylenediamine oxalate and $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ in 20% and 25% of H_2SO_4 , respectively. 0.5% diammonium hydrogen phosphate solution was prepared by dissolving appropriate mass of $(\text{NH}_4)_2\text{HPO}_4$ in deionized water. Working solutions were prepared daily by dilution of the stock solutions. Ethyl and butyl mercaptans (Sigma-Aldrich, USA) solutions were prepared by dilution an aliquot of each compound in methanol.

The palladium complex (PdA_2) is sparingly soluble in methanol. A stock solution was prepared by adding 25 mL of methanol to a flask containing 5 mg of PdA_2 and stirring vigorously. For the reagent, 2 mL of stock solution was added to a 25 mL volumetric flask and the volume was completed with methanol. The reagent was stable for around 8 h and was therefore prepared daily.

2.3. Analytical procedure

An aliquot of 2.0 mL of sulfide solution was added in a 5 mL volumetric flask. In sequence was add 500 μL of reagent solution with gentle swirling, and diluted to 5 mL with deionized water. The mixture was allowed to stand at room temperature for approximately 2 min. The fluorescence intensity of the solution was then measured against a reagent blank, using a 1.0 cm path length cell and excitation (λ_{ex}) and emission (λ_{em}) wavelengths of 245 nm and 410 nm, respectively.

3. Results and discussion

3.1. Structural characterization

2-Aminobenzoic acid can bind to palladium in coordination modes including monodentate O and N bridging or chelation involving nitrogen and the oxygen atom of the hydroxyl group, forming a six-member chelate ring [30].

The bending frequency of the NH_2 group, $\delta(\text{NH}_2)$, of 2-aminobenzoic acid was located at 1586 cm^{-1} , while that of PdA_2 was at 1557 cm^{-1} , giving a frequency shift of 29 cm^{-1} . 2-Aminobenzoic acid showed two

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